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Green Approach towards Corrosion Inhibition in Hydrochloric Acid Solutions

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Abstract: The influence of *Hyssopus officinalis* (L), (Hyssop), or (Zoufa) on the corrosion of mild steel and zinc alloy in 0.5 M HCl solution was tested through open circuit potential-time measurements (OCP), potentiodynamic polarization, as well as electrochemical impedance spectroscopy (EIS) techniques. *Hyssop* leaf extract exhibited good inhibition efficiency in HCl solutions for both metals. To determine the nature of interaction among the leaf extract and both metallic surfaces, the experimental data have been tested with several adsorption isotherms. The thermodynamic activation parameters were calculated. The data showed that the adsorption process on both metals occurs through a physical adsorption mechanism. *Hyssopus officinalis* (L) leaf extract can be suggested as an effective green inhibitor of corrosion of mild steel and zinc alloy in HCl solutions.

Keywords: mild steel; zinc alloy; EIS; leaf extract; hydrochloric acid; corrosion inhibition.

1. Introduction

Zinc alloy is a desirable commodity in the corrosion sector due to various industrial applications, including chargeable batteries and steel galvanizing for corrosion safety [1, 2]. It is often used as a sacrificial metal in coatings to protect other metals, particularly ferrous metals [3]. Mild steel is also used in numerous applications as flow lines, constructions of tanks, and petroleum refinery equipment owing to its simple fabrication process and low cost. Yet, both metals are susceptible to corrosion and degradation, particularly in acidic media. HCl is the most widely used acid in metal pickling and descaling processes [2-9]. Organic inhibitors, whose molecules appear to adsorb on the metal surface, are among the best methods to protect metals from corrosion [10-12]. Although their application seems an effective, easy technique, most of them are non-biodegradable and vastly poisonous for human beings and the environment. So far, for environmental and safety reasons, much consideration has been focused on finding low-priced non-toxic green inhibitors [4, 5, 13-19]. Many research studies have attempted to evaluate naturally occurring plant extracts as corrosion inhibitors for different metals. [4, 5, 13-24]. Their efficiencies were estimated to be around 55-90% in acidic media.

Hyssopus officinalis (L) (Hyssop) is an East Mediterranean herb that is commonly used as herbal remedies as well as food spices. It was reported that the leaves of this minty flavor herb contain a variety of polyphenolic compounds, such as quercetin, diosmin, luteolin, as well as chlorogenic ferulic, syringic, and caffeic acids [25].

The current research aims to study the difference in the electrochemical corrosion behavior of zinc alloy and mild steel in HCl solutions in the presence of *Hyssop* leaf extract. Moreover, we pursue to shed light on the mechanism of inhibition of the extract and its thermodynamic parameters.

2. Materials and Methods

2.1. Solution preparation and extraction procedure.

0.5 M HCl (Scharlau chemical industries) solutions, as well as *Hyssop* leaf extract solution, were obtained similar to those reported previously [4,5,14].

2.2. Electrochemical studies.

Electrochemical impedance (EIS) and polarization measurements were obtained through frequency response analyzer (FRA)/potentiostat supplied from ACM instruments (UK). A detailed description of the used cell setup and conditions were described earlier [4, 7]. The chemical composition of the zinc alloy was (wt. %) (Zn: 94.46, Si: 0.49, Br:1.15, Mo: 0.64, and Fe: 0.75) while that of mild steel the same as the one tested with Al-Moghrabi *et al*. [4, 5].

3. Results and Discussion

3.1. Open circuit potential measurements (OCP).

Open Circuit Potential (OCP) is a passive technique known as open-circuit voltage, zero-current potential, corrosion potential, equilibrium potential, or rest potential. It is often used to find the resting potential of a system, from which other experiments are based. Figure 1 shows that the OCP of zinc alloy and mild steel electrodes in 0.5 M HCl solutions were shifted towards more positive values in the presence of 0.5 g. L^{-1} *Hyssop* leaf extract. This positive shift shows that Hyssop leaf extract's presence impacts the anodic dissolution of both metals [4, 5]. *Hyssop* leaf extract can be classified as a mixed type inhibitor since the change of the corrosion potential (E_{corr}) values for both metals in the absence and presence of the extract is lower than 85 mV [8].

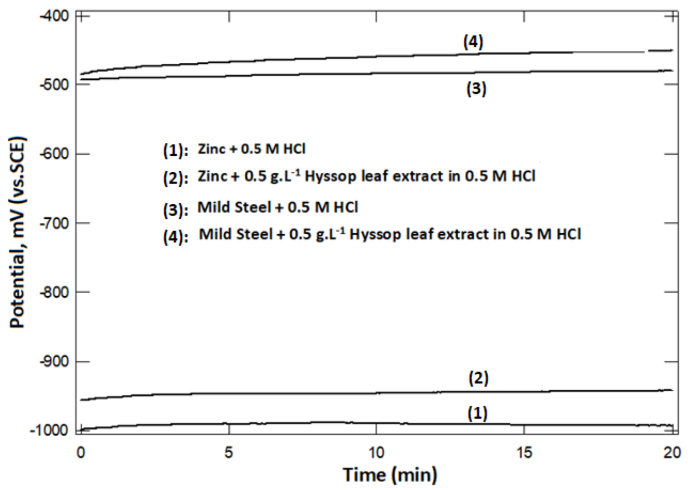

Figure 1. Variation of open circuit potential as a function of time for zinc alloy and mild steel electrodes in 0.5 M HCl solution in the absence and presence of 0.5 g. L^{-1} *Hyssop* leaf extract at 30°C.

3.2. Potentiodynamic polarization data measurements.

Potentiodynamic polarization is one of the electrochemical techniques used in laboratories for corrosion testing. This technique gives information on the corrosion rate, corrosion mechanism, and the vulnerability of certain materials in specific environments to corrosion.

The potentiodynamic polarization curves depicted in Figures 2 (a and b) indicate that *Hyssop* leaf extract suppresses both anodic and cathodic Tafel reactions, confirming that it acts as a mixed-type inhibitor the corrosion of mild steel and zinc alloy in 0.5 M HCl solutions.

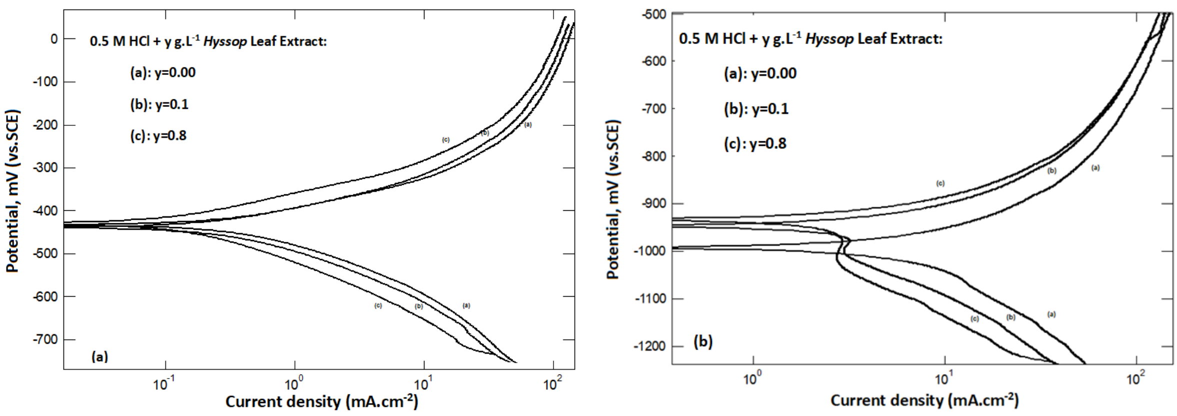

Figure 2 (a and b). Potentiodynamic polarization curves for zinc alloy and mild steel in 0.5 M HCl in the absence and presence of different concentrations of *Hyssop* leaf extract at 30°C.

The electrochemical parameters, including the corrosion current density (i_{corr}) and the inhibition efficiency (η) are given in Table 1. The η was obtained from polarization measurements using equation (1):

$$\eta = [(i_0-i)/i_0] \times 100 \quad (1)$$

Where i_o and i, are the corrosion current densities in the absence and the presence of *Hyssop* leaf extract, respectively.

The tabulated data revealed that increasing *Hyssop* leaf extract concentrations reduces i_{corr} values and consequently increases η. The slight variations in anodic and cathodic Tafel slopes, β_a and β_c, in the presence of *Hyssop* leaf extract in both metals suggest that the inhibiting action is occurring by blocking current cathodic and anodic sites on the metal surface. *Hyssop* leaf extract could be classified as a pickling-type inhibitor in both metals since it does not affect their corrosion potential (E_{corr}) [4, 5].

Table 1. The electrochemical polarization parameters for the corrosion of zinc alloy and mild steel in 0.5 M HCl containing different concentrations of *Hyssop* leaf extract respectively at 30°C.

Metal	Conc (g.L^{-1})	E_{corr} (mV vs. SCE)	β_a (mV/decade)	β_c (mV/decade)	i_{corr} (mA. cm^{-2})	η
Zinc alloy	**Blank**	-1001	189	240	7.070	-
	0.100	-1016	195	153	3.412	53
	0.200	-1005	172	178	2.900	59
	0.600	-1000	159	199	2.454	65
	0.800	-1005	166	198	2.288	68
Mild Steel	**Blank**	-453	74	106	0.541	-
	0.100	-435	66	100	0.253	53
	0.200	-429	68	101	0.206	62
	0.600	-428	67	93	0.139	74
	0.800	-423	65	103	0.109	80

3.3. Electrochemical impedance spectroscopy results.

EIS is a perturbative characterization of the dynamics of an electrochemical process. It is a non-destructive alternating current method used to measure the corrosion rate of different materials. Owing to its ability to reveal a vast number of physical and electronic properties such as diffusion coefficients, electron transfer rate constants, adsorption mechanisms, charging resistance, capacities, and pore sizes, the application of EIS has significantly increased over recent years, particularly in corrosion fields, coatings sector as well as battery fuel cells. Figures 3a represent the bode theta spectra of zinc alloy and mild steel in the absence and presence of 0.5 g. L^{-1} *Hyssop* leaf extract.

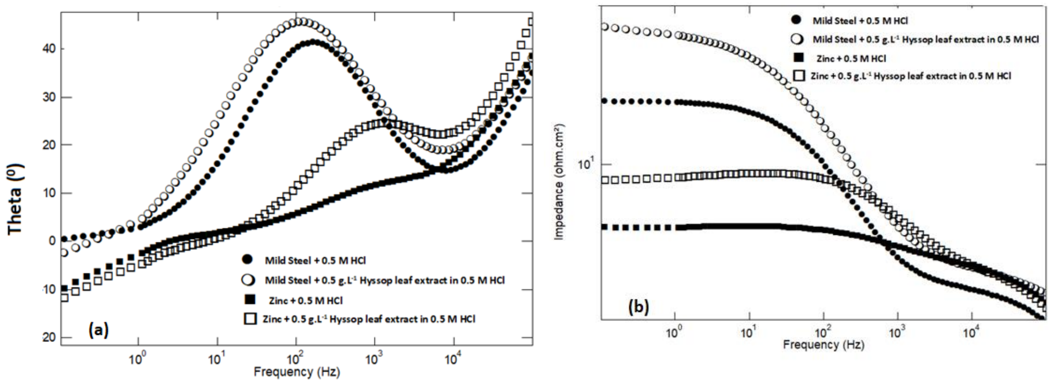

Figure 3 (a and b). Bode theta (a) and Bode impedance spectra (b) of zinc alloy and mild steel in the absence and presence of 0.5 g. L^{-1} *Hyssop* leaf extract.

As seen, the plots of mild steel exhibit one maximum, i.e., only one time constant at the intermediate frequencies, while the zinc alloy plots clarify the presence of two overlapped time constants. The phase angle values are less than 90°, suggesting the existence of inhomogeneities in the system [26]. Moreover, these values in both metals increase with the addition of *Hyssop* leaf extract. Such increase may be accredited to the decrease in the capacitive behavior at the mild steel and zinc alloy surfaces due to the reduction of their dissolution rate in the presence of *Hyssop* extract [27].

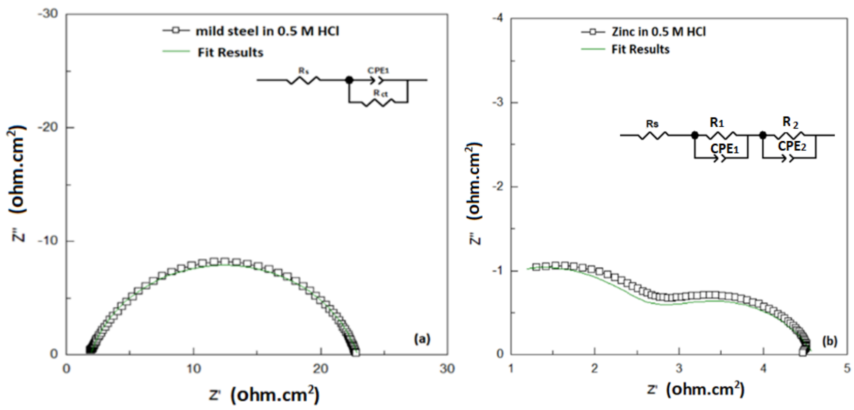

Figure 4 (a and b). The experimental and computer fit results as well the equivalent circuit model of Nyquist plot of blank 0.5 M HCl with mild steel (a) and zinc alloy electrodes (b).

Figure 3b shows that the modulus impedance obtained at minimum frequency Z_{min} rises with the addition of 0.5 g. L^{-1} *Hyssop* leaf extract for both mild steel and zinc alloy. Z_{min} has been reported to show a similar trend as the charge transfer resistance (R_{ct}) [26]. Thus, it can be used to evaluate Hyssop leaf extract's inhibition efficiency on the corrosion of zinc alloy and mild steel. The experimental, computer fit results and the equivalent circuit models of

Nyquist plots of blank 0.5 M HCl in mild steel (a) and zinc alloy (b) are depicted in figures 4 (a and b).

The inset of Figures 4a and 4b comprises the solution resistance (R_s), the constant phase elements (CPE_1 and CPE_2), the resistance R_1 and R_2. It is worth mentioning that in the inset of 4a, R_2 denotes the charge transfer resistance element (R_{ct}), whereas in 4b, (R_1+R_2) represents the total charge transfer resistance (R_{ct}). Both figures show characteristic depressed capacitive semicircles, suggesting that mild steel and zinc alloy dissolution occur under activation control. The depressed semicircles are attributed to metal surface roughness [2,4,5]. The Nyquist impedance plot of mild steel, Figure 4a, includes one depressed semicircle suggesting single charge transfer [28]. However, figure 4b is characterized by the presence of two depressed capacitive loops; the first was partially viewed, due to the high frequencies limit of the instrument, with a diameter (resistance) R_1, and the other one was noticed at medium and low-frequency domains with high resistance, R_2. The total R_{ct}, equals (R_1 + R_2). Such a model has been applied to characterize 3-D inhomogeneous layer systems [29]. The high-frequency capacitive loop is attributed to the time constant of charge-transfer and double-layer capacitance [30-32]. The second time constant (the low-frequency capacitive loop) is related to a step in the dissolution process.

The inhibition efficiency (η) can be obtained from impedance measurements according to equation (2):

$$\eta = [(R_{ct} - R_{ct0})]/R_{ct} \times 100 \qquad (2)$$

Where, R_{ct0} and R_{ct} are the values of the charge transfer resistance (Ω cm^2) in the absence and the presence of *Hyssop* leaf extract, respectively.

The electrochemical impedance parameter values obtained from such fitting are presented in Tables 2 and 3.

Table 2. The electrochemical impedance parameters for the corrosion of mild steel in 0.5 M HCl containing different concentrations of *Hyssop* leaf extract at 30 °C.

Metal	Conc. ($g.L^{-1}$)	R_s (Ω cm^2)	R_2=R_{ct} (Ω cm^2)	Y_0 =$Q_{dl\ 2}$ $\mu s^n/\Omega\ cm^2$	$C_{dl\ 2}$ $\mu F/cm^2$	n_2	η
Mild Steel	**Blank**	1.9	20.6	367	2607	0.82	-
	0.100	2.4	28.5	338	2531	0.82	28
	0.200	2.6	38.5	374	2317	0.84	46
	0.300	2.7	43.8	339	2112	0.84	53
	0.400	2.7	48.6	309	2215	0.83	58
	0.500	2.8	50.6	337	2156	0.84	59

In a non-homogenous system, the capacitances were applied as a Constant Phase Element (CPE) that is defined by the non-ideal-double layer capacitance, Q, and constant n.

The impedance, Z, of CPE is represented using equation (3):

$$Z_{CPE}=Q^{-1}(i\omega)^{-n} \qquad (3)$$

where $i = (-1)^{1/2}$, ω is the frequency in rad s^{-1}, ω = 2Πf, and f is Hz's frequency. When n values are less than unity, Q has units of $\mu s^n/\Omega cm^2$, which is correlated to CPE admittance (Y_0). The ideal double-layer capacitance (C_{dl}) could be calculated using equation (4)[4, 8].

$$C_{dl}= \frac{(Y_o\ x\ R_{ct})^{1/n}}{R_{ct}} \qquad (4)$$

It's evident from the tabulated data that increasing *Hyssop* leaf extract concentration increases the R_{ct} values and decreases C_{dl} values, leading to increased η values. n_1 values indicate the type of ideal semicircle, while the values of n_2 indicate depressed ones [7].

Table 3. The electrochemical impedance parameters for the corrosion of zinc alloy in 0.5 M HCl containing different concentrations of *Hyssop* leaf extract at 30 °C.

Metal	Conc. ($g.L^{-1}$)	R_1 (Ω cm^2)	Q_1 (μF cm^{-2})	n_1	R_2 (Ω cm^2)	$Y_0 = Q_{dl\,2}$ $\mu s^n/\Omega$ cm^2	$C_{dl\,2}$ (μF cm^{-2})	n_2	η
Zinc alloy	**Blank**	2.3	2.75	0.91	2.0	1070	18246	0.73	-
	0.002	2.0	1.48	0.96	2.6	700	11242	0.73	6.52
	0.005	2.0	1.88	0.96	3.8	800	21167	0.71	25.86
	0.01	2.2	1.49	0.97	4.1	570	6602	0.76	31.74
	0.05	2.4	7.50	0.84	4.2	280	1322	0.82	34.84
	0.100	2.4	3.00	0.91	4.9	190	578	0.86	41.09
	0.200	2.5	2.11	0.94	5.0	190	580	0.86	42.66
	0.300	2.2	0.67	0.99	5.8	200	767	0.84	46.25
	0.500	2.1	1.51	0.97	6.9	160	551	0.85	52.22

Potentiodynamic polarization measurements were used to calculate the degrees of surface coverage values (θ = η/100) presented in figure 5. The curves indicate that the efficiency increases with an increase in the extract's concentration up to a threshold concentration, after which a slight increase is achieved. Such behavior suggests the development of monolayer films on mild steel and zinc alloy surfaces. It is noted that Hyssop leaf extract is more efficient in mild steel than in zinc alloy at any concentration.

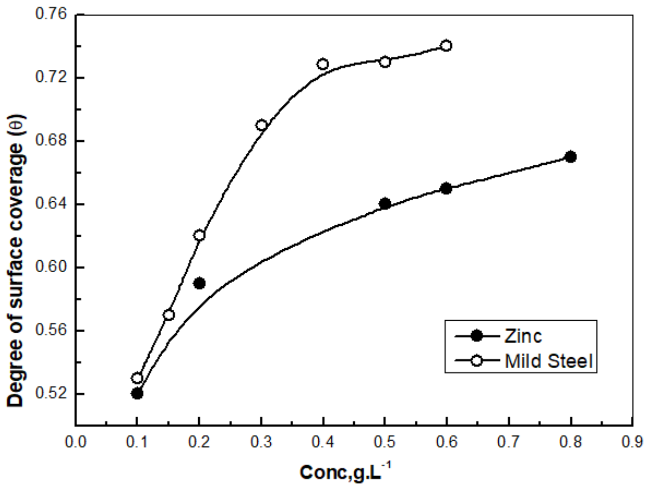

Figure 5. Variations of a degree of surface coverage of mild steel and zinc alloy with different concentrations of *Hyssop* leaf extract in 0.5 M HCl solutions at 30°C.

The slight difference of η obtained from impedance and polarization measurements may be attributed to the fact that, in EIS, the corrosion rate is taken as the reciprocal of R_{ct}. This assessment is based on the fact that cathodic and anodic slopes are constant within the concentration studied. Therefore, η obtained from polarization and impedance measurements will be in good agreement with each other if i_{corr} is identical to ($1/R_{ct}$). This will takes place only if the constant $\frac{(\beta_a \cdot \beta_c)}{2{\cdot}303(\beta_a+\beta_c)}$ equal unity [14].

3.4. Adsorption isotherms.

The corrosion inhibition relies on the surface conditions and the inhibitors' mode of adsorption [14]. An inhibitor's action is attributed to adsorption at the metal/solution interface as a primary substitution step in the corrosion inhibition. Such adsorption might occur via electrostatic attraction between the charged metal and the charged inhibitor molecules or dipole-type interaction between unshared electron pairs in the inhibitor with the metal or π-Interaction between **i**nhibitors with multiple or conjugated π-bonds and the metal. Table 4 shows the fitting of θ obtained from potentiodynamic polarization at different concentrations to Langmuir, Kinetic-Thermodynamic model, and Florry–Huggins isotherms [4, 5, 7].

Table 4. Linear fitting parameters of *Hyssop* leaf extract according to all isotherms in mild steel and zinc alloy surfaces in 0.5 M HCl at 30 °C.

Inhibitor	Kinetic Model			Florry Huggins		
	K	1/y	R^2	K	x	R^2
Zinc alloy	14.76	3.46	0.98	45.45	5.06	0.98
Mild steel	11.10	1.54	0.98	10.46	1.81	0.96

It was found that the Langmuir isotherm is unsuitable for fitting the data of *Hyssop* leaf extract in mild steel and zinc alloy, indicating that there may be non-ideal behavior in the adsorption processes of *Hyssop* leaf extract on mild steel and zinc alloy surfaces [33]. The non-ideal behavior of *Hyssop* leaf extract molecules on both metals is confirmed by the values of the number of active sites occupied by a single inhibitor molecule, 1/y, and x the size parameter, which are more than unity, indicating that each active molecule of *Hyssop* extract was adsorbed onto more than one active site. Accordingly, the adsorbed molecules on the zinc alloy and mild steel surfaces are bulky [2, 4, 5, 7].

It is worth mentioning that the inhibition efficiency of an inhibitor relies on the value of binding constant K_{ads}, which denotes the strength between the adsorbed inhibitor's species and the metal surface [2, 4, 5, 7]. Though, numerical values of K are greater with the zinc electrode than with the mild steel, contrary to experimental results. Such difference may be due to the strong adsorption of *Hyssop* leaf extract molecules on the whole zinc surface.

ΔG_{ads} values were obtained from the kinetic thermodynamic model as reported previously [4, 7, 8, 14]. They were -16.89 and -16.18 $kJ.mol^{-1}$ for zinc alloy and mild steel in 0.5 M HCl solutions, respectively. Such values reveal the spontaneity of Hyssop leaf extract's adsorption process on mild steel and zinc alloy and the stability of the adsorbed layers on both metals in the 0.5 M HCl solution. ΔG_{ads} values indicate that the adsorption process on both metals occurs via a physical adsorption mechanism [4, 5].

3.5. Activation and thermodynamic parameters.

The activation and thermodynamic parameters are of countless significance for elucidating the mechanism of corrosion inhibition of metals. Figure 6 shows that increasing the temperature reduces the size of the depressed semicircles, indicating a decrease in R2 values of R2 values and, consequently, in Rct values, thus increasing the corrosion rate. Such behavior approves the desorption of *Hyssop* extract molecules from the zinc alloy at elevated temperatures. Likewise, observation is reported with the mild steel electrode.

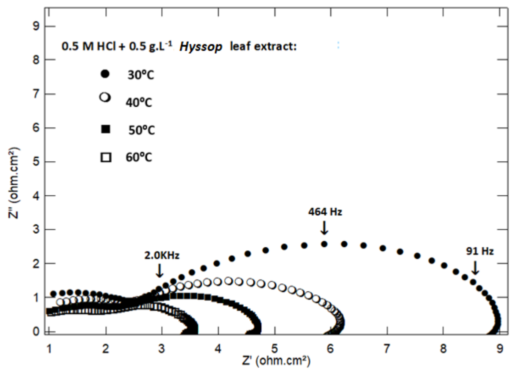

Figure 6. Nyquist Impedance plots for zinc alloy in 0.5 M HCl in the presence of 0.5 $g.L^{-1}$ *Hyssop* leaf extract at different temperatures.

The activation parameters for zinc alloy and mild steel in 0.5 M HCl in the absence and presence of 0.5 and 0.6 g.L^{-1} *Hyssop* leaf extract were obtained from the linear square fitting of ln(υ) and ln (υ/T) data vs. (1/T), by applying Arrhenius and transition state equations [4, 5]. The corrosion rates (υ) were taken as i_{corr} that were obtained from the potentiodynamic polarization curves of zinc alloy and mild steel in 0.5 M HCl in the absence and presence of 0.5 and 0.6 g.L^{-1} *Hyssop* leaf extract. Figures 7 and 8 show the application of Arrhenius and transition state equations for zinc alloy and mild steel in 0.5 M HCl in the absence and the presence of 0.5 and 0.6 g. L^{-1} *Hyssop* leaf extract acid in zinc alloy and mild steel, respectively. The apparent activation energy, E_a, activation entropies, ΔS*, and activation enthalpies, ΔH*, in the absence and presence of *Hyssop* extract are depicted in Table 5.

It is clear that E_a and ΔH* values decrease for mild steel, revealing that rising temperature slightly affects the effectiveness of *Hyssop* leaf extract [34]. However, they increase in zinc alloy, indicating a higher protection efficiency. The positive values of ΔH* and negative entropy of activation, ΔS* values indicate that the activated complex's formation is an endothermic ordered associative step [4,5].

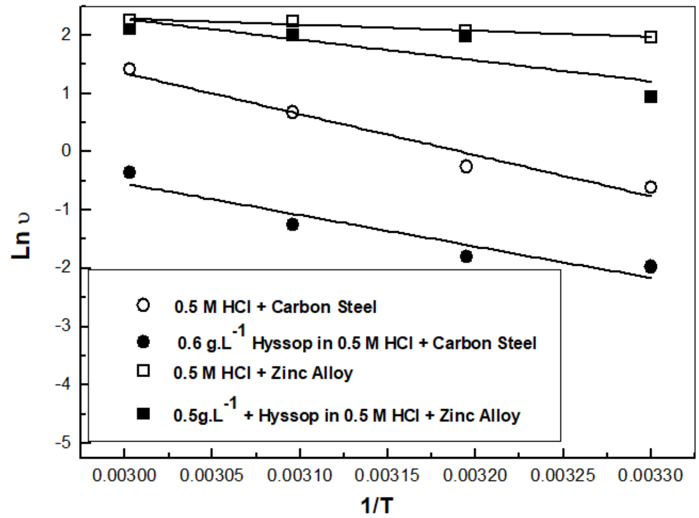

Figure 7. Application of Arrhenius equation on mild steel and zinc alloy in 0.5 M HCl in the absence and the presence of 0.6 and 0.5 g. L^{-1} *Hyssop* leaf extract, respectively.

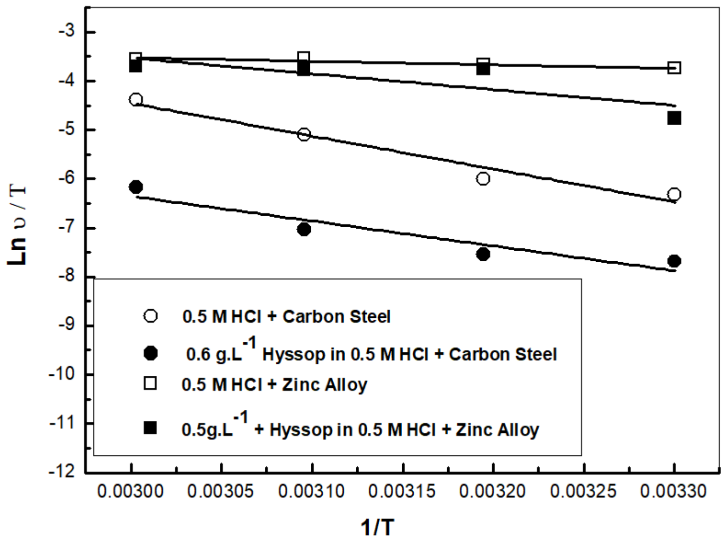

Figure 8. Application of transition state equation on mild steel and zinc alloy in 0.5 M HCl in the absence and the presence of 0.6 and 0.5 g. L^{-1} *Hyssop* leaf extract, respectively.

Table 5. The activation parameters of mild steel and zinc alloy in 0.5 M HCl in the absence and the presence of 0.6 and 0.5 g. L^{-1} *Hyssop* leaf extract respectively.

Metal	E_a kJ.mol^{-1}	ΔH* kJ.mol^{-1}	ΔS* J.mol^{-1}.K^{-1}
Zinc Alloy	8.75	6.10	-209
Zinc alloy +0.5 g.L^{-1} *Hyssop*	29.55	26.92	-146
Mild Steel	58.53	55.89	-61
Mild Steel +0.6 g.L^{-1} *Hyssop*	44.85	42.21	-124

4. Conclusions

Mild Steel and zinc alloy have different electrochemical impedance behavior in an acidic solution containing *Hyssop* leaf extract. *Hyssop* leaf extract inhibits the corrosion of mild steel and zinc alloy via a physical adsorption mechanism.

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Conflicts of Interest

The authors declare no conflict of interest.

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